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(54) **POROUS SEMICONDUCTOR MATERIAL**
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(73) Proprietor: **QinetiQ Limited**
London, SW1 6TD (GB)

(72) Inventor: **CANHAM, Leigh, Trevor**
Worcs WR14 3PS (GB)

(74) Representative: **Bowdery, Anthony Oliver**
QinetiQ Group plc, Cody Technology Park, IP
Formalities, A4 Bldg, Rm G016, Ively Road
Farnborough, Hants GU14 0LX (GB)

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Description

[0001] This invention relates to porous semiconductor material such as silicon in particular, although not exclusively, to methods of producing such material and to devices incorporating it.

[0002] In recent years great interest and considerable research and development activity has been generated in response to the discovery of visible luminescence at room temperature from porous silicon. There have been a substantial number of publications in the scientific literature and also patent applications. See for example the 1992 Fall Meeting of the Materials Research Society, the symposium being entitled "Microcrystalline Semiconductors..Materials Science and Devices", November 30 to December 4, 1992. International Patent Applicant No PCT/GB90/01901 published as WO 91/09420 relates to porous silicon having luminescent properties by virtue of its containing silicon quantum wires. Bulk (ie non-porous) silicon has very poor luminescence efficiency because it has indirect gap band structure. Highly porous silicon containing silicon quantum wires has much greater luminescence efficiency, and the luminescence emission is of shorter wavelength. Luminescence is associated with quantum confinement of charge carriers within quantum wires of which the porous silicon is composed.

[0003] Experience has shown that the luminescence properties of porous silicon improve both with increasing porosity and with increasing resistivity of the original p-type bulk silicon starting material from which the porous silicon is produced. However, the structural properties of conventionally produced porous silicon degrade with both increasing porosity and increasing starting material resistivity. In Appl. Phys. Lett. Vol 60 (18), pages 2285-2287, 4 May 1992, Friedersdorf et al. discuss the influence of stress on porous silicon luminescence. They show in Figure 2 an optical micrograph of porous silicon exhibiting "cellular structure", this being the crazing and cracking of porous silicon material. A substantial degree of delamination or peeling of the porous silicon occurs. This makes high porosity porous silicon structurally unsuitable for luminescent device applications. It is too mechanically weak at porosities high enough to provide useful luminescence. Experience shows that porous silicon produced in accordance with International Patent Application No PCT/GB90/01901 begins to exhibit crazing and partial disintegration at porosities above 90% for bulk silicon starting material of resistivity not greater than 10^{-2} ohm cm (p⁺ type) and porous layer thickness of 4 μ m or greater. Here the porosity is determined gravimetrically assuming no shrinkage during production. The situation is worse with higher resistivity p type silicon starting material (p⁺, 1 ohm cm). Here crazing and partial disintegration occur at gravimetric porosities above 80% and layer thicknesses similar to the p⁺ equivalents.

[0004] Difficulties in producing high porosity silicon

are also shown by Lehmann et al., Mat. Res. Soc. Symp. Proc. Vol. 283, pages 27-32, 1993. Figure 6 of this article demonstrates crack evolution and shrinkage during production. Similar effects were also mentioned in a paper by Beale et al. J. Cryst. Growth, Vol. 73, p622 onwards 1985. This paper describes low density porous silicon films which craze and peel during production. In a very recent paper by Grivickas et al., Thin Solid Films, Vol 235, p.234, 1993, it is stated that the thickest porous silicon films broke off from the substrate and disintegrated into small pieces. It is consequently a long felt want to provide high porosity semiconductor material such as silicon with good structural characteristics.

[0005] Luminescent porous silicon layers having thicknesses in the range 20 μ m to 80 μ m are described by Badoz et al. in the Materials Research Society Symposium Proceedings, Volume 283, 1993, pages 97 to 108. Similar porous silicon material is reported by Sagnes et al. in Applied Physics Letters, Volume 62(10), 1993, pages 1155-1157. Prior art techniques for the fabrication of thick luminescent porous silicon layers are known to result in structures in which only a top layer of the porous silicon is luminescent.

[0006] It is an object of the invention to provide porous semiconductor material of improved structure and a method of making it.

[0007] The present invention provides porous semiconductor material according to claim 1 which is at least partly crystalline, characterized in that the semiconductor material has a porosity in excess of 90% determined gravimetrically and in that the porous semiconductor material has one or more of the following properties :

- there are substantially no voids, crazing and peeling discernible in the semiconductor material by scanning electron microscopy at a magnification of 7,000;
- the semiconductor material has a crack density of less than 10^8 cm⁻²;
- the semiconductor material is free of cracks greater than 0.1 μ m in width.

[0008] The invention provides the advantage that the material is of much higher structural quality than in the prior art of high porosity crystalline semiconductor materials.

[0009] In a further aspect, the invention provides a method of making porous semiconductor material according to claim 22, incorporating the step of producing porous semiconductor material which is liquid-wetted and at least partly crystalline, characterized in that the method further incorporates the step of drying the porous semiconductor material by a supercritical drying process.

[0010] Preferred embodiments are set out in the appended claims.

[0011] In order that the invention might be more fully understood, examples thereof will now be described,

with reference to the accompanying drawings, in which:-

- Figure 1 schematically shows a silicon substrate wafer and a porous silicon layer thereon;
- Figure 2 schematically shows apparatus for supercritical drying;
- Figure 3 to 6 are drawings produced from scanning electron microscope photographs of porous silicon material dried in air and dried by a supercritical drying process;
- Figure 7 is a drawing of a transmission electron diffraction pattern from porous silicon material produced in accordance with and of the invention;
- Figure 8 shows photoluminescence spectra obtained from a porous silicon specimen of the invention and a comparison specimen;
- Figure 9 shows measured data and theoretical model data obtained by spectroscopic ellipsometry for a porous silicon specimen of the invention and a comparison specimen; and
- Figure 10 shows photoluminescence data from a porous silicon specimen of the invention.

[0012] Referring to Figure 1, a Czochralski-grown (cz) single crystal silicon wafer 10 350 μm in thickness is shown in section. Chain lines 11 indicate that the wafer 10 is illustrated on a reduced scale. The wafer 10 has a surface layer 12 of porous silicon material thereon of 4.5 μm thickness. The layer 12 has an upper surface 14 remote from the wafer 10. Strictly speaking the expression "layer" is a misnomer, although it is often used in lithography.

[0013] The layer 12 was not "laid down"; it was produced electrochemically by an anodizing/etching process, ie anodization combined with etching. The wafer 10 was of heavily doped p-type (p^+) silicon material, with a resistivity in the range 5×10^{-3} ohm cm to 15×10^{-3} ohm cm.

[0014] The wafer 10 was anodized in what is referred to as "10% ethanoic" hydrofluoric acid (HF) solution; this produced small pores in the wafer 10, which was then subjected to etching by soaking in the same solution. The etching produced pore overlap defining silicon quantum wires. The ethanoic HF solution was produced from an aqueous solution of 20% by weight of HF in water, this solution being subsequently mixed with an equal volume of ethanol. The resulting mixture is referred to

as 10% ethanoic HF solution.

[0015] Anodization of the wafer 10 was carried out in the 10% ethanoic HF solution at a current density of 50 mAcm^{-2} for 3 minutes. An anodizing/etching apparatus was employed as described in International Patent Application No PCT/GB90/01901 previously mentioned. This anodization produced a substantially uniform gold coloured porous layer (or stratum of porous silicon material) which is $4.5 \pm 0.5 \mu\text{m}$ in thickness. The layer had a porosity (void fraction) of 85%, ie its density was 15% that of non-porous crystalline silicon.

[0016] In accordance with the invention it is desired to produce a layer 12 with porosity of at least 90%. Moreover, it is desired that the layer 12 remain crystalline and continue to be supported by the non-porous substrate or wafer 10. In International Application No. PCT/GB90/01901 referred to above, a procedure is disclosed in which silicon is anodized and subsequently etched to increase porosity. However, it has been found that etching to a porosity in excess of 90% creates porous silicon, which, upon drying to remove the etchant, exhibits at least partial disintegration by cracks, crazing and peeling of the porous layer from the substrate.

[0017] The porous layer 12 was subjected to chemical dissolution (etching) for 30 minutes in 10% ethanoic HF solution (as used for anodization). This increased its porosity to an average value of 95% (measured by gravimetric analysis). The layer 12 was maintained in a wet state (ie wetted by the ethanoic HF etchant solution), and was transferred in this state to a bath of pure ethanol with etchant initially within its pores. The wafer 10 and layer 12 were cleaved under the ethanol to provide reduction to a size suitable for insertion within a pressure vessel. The cleaved wafer was then transferred to a pressure vessel of 50 ml volume. The wafer remained in an ethanol-wetted state during transfer, and the vessel itself was full of ethanol.

[0018] Referring now also to Figure 2, there is shown in schematic form an apparatus 20 for supercritical drying of materials. The apparatus 20 incorporates a CO_2 input pipe 22 connected to a pump 24 with a chilled (8°C) pump head (not shown). The pipe 22 connects the pump 24 to a CO_2 reservoir (not shown); the pump 24 is connected to a pressure vessel 26 within an oven 28. The vessel 26 is connected to a back pressure regulator 30 with an outlet 32 to an effluent receiver vessel 34.

[0019] In operation of the apparatus 20, the wafer was within the pressure vessel 26. The ethanol and residual electrolyte within the pores of the layer 12 was replaced by liquid CO_2 supplied to the pressure vessel 26 by means of the pump 24. The liquid CO_2 flushed the ethanol from the layer pores. It was pumped through the pressure vessel 26 at a flow rate of 2 cm^3 per minute, a temperature of 18°C and a pressure of 1500 psi (10.1 MPa). The level of ethanol remaining in the layer pores was monitored by sampling and analysing effluent from the outlet 32. After flushing with liquid CO_2 for 3 hours, there was less than 10ppm of ethanol in the effluent.

[0020] The pressure vessel 26 containing the wafer 10 immersed in liquid CO₂ was then subjected to increased temperature by means of the oven 28. The temperature within the vessel 26 was increased at 1°C per minute to 40°C, and the pressure rose gradually to 2400 psi (16.2 MPa). At this point the CO₂ was a supercritical fluid, ie a fluid above its critical point. The pressure was then reduced to 1500 psi (10.1 MPa), and supercritical CO₂ was flushed through the pressure vessel 26 at 40°C for 2 hours. Maintaining the pressure vessel temperature at 40°C, the CO₂ was slowly vented from the vessel 26 over a period of 16 hours reducing the pressure within the vessel to atmospheric. On removal from the vessel 26, the porous silicon layer was found to be substantially free of disintegration by cracks, peeling or crazing. It had a porosity (void fraction) of 95% as determined by gravimetric analysis. The specimen produced in this way is referred to as UHP 23A. The silicon wafer (in a wet state and with etched porous layer) from which UHP 23A was cleaved was dried by being allowed to stand in air as in the prior art. This wafer was then designated comparison specimen UHP 23.

[0021] The morphologies of supercritically dried specimen UHP 23A and air dried comparison specimen UHP 23 were investigated as follows. A scanning electron microscope (SEM) was employed to study the upper surfaces of these specimens, ie the equivalents of the surface 14 in Figure 1 remote from the wafer 10. Figures 3 and 4 are drawings reproduced from such micrographs for specimen UHP 23 and specimen UHP 23A respectively. Figure 3 is reminiscent of fissured dried mud; it has a magnification in the region of 1.4×10^3 ; this is indicated by a line 30 having a length corresponding to 10 µm in physical distance. Figure 3 shows that air dried specimen UHP 23 consists of regions of porous silicon such as 32 (unshaded) alternating with fissures such as 34 (shaded). The fissures 34 are of greater total surface area than the silicon regions 32, and are up to 8 µm in width. The silicon regions 32 are typically 2 µm to 5 µm in width. In contrast, Figure 4 is a plain featureless scene; UHP 23A exhibited no recognisable cracks, fissures, or other morphology in the SEM photograph. In Figure 4 a line 40 corresponds to a physical length of approximately 1 µm, indicating a magnification in the region of 7×10^3 . Figure 4 thus illustrates an area of porous silicon of approximately 20 µm x 10 µm. In consequence, cracks less than 0.1 µm wide would have been visible if present. Specimen UHP 23A is therefore free of cracks greater than 0.1 µm in width.

[0022] The specimens UHP 23 and UHP 23A were cleaved perpendicular to their upper surfaces (14 in Figure 1), and SEM photographs were taken of the cleavage surfaces. Figure 5 (UHP 23) and Figure 6 (UHP 23A) were drawn from such photographs; they represent magnifications of about 7×10^3 as indicated by respective lines 50 and 60 corresponding to physical lengths of 1 µm. Figures 5 and 6 show porous silicon layers 52 and 62 upon respective wafer substrates 54

and 64. The layer 52 of the air dried specimen UHP 23 has substantial void or fissure regions 56, 2 µm and 5 µm across, interspersed with porous silicon material 58, 8 µm across. The layer 62 of the supercritically dried specimen UHP 23A has no visible voids or fissures and is of substantially constant thickness. This shows that supercritical drying has substantially obviated the shrinkage and cracking of prior art porous silicon. From the photographs used to prepare Figures 4 and 6, the crack density is less than 10^8 cm^{-2} .

[0023] In order to investigate the crystallinity of supercritically dried specimen UHP 23A, a transmission electron diffraction pattern was obtained using a 300 kV electron beam. Flakes of porous silicon were removed from UHP 23A and introduced into the electron diffraction instrument. Figure 7 was drawn from the resulting photograph. It shows inter alia a central undiffracted beam 70 with four first order diffraction lobes 72. The lobes 72 are characteristic of the 110 orientation of crystalline silicon. Second order or (220) orientation lobes 74 are also shown. There is no evidence for the presence of randomly oriented crystallites, since there are no diffraction rings. In the photograph from which Figure 7 was produced, there was a small amount of background intensity (not shown) in the region 76 between the central beam 70 and first order lobes 72. Such background can arise from a number of phenomena, one of which is the presence of amorphous material, in this case SiO₂. The background was sufficiently weak in intensity compared to the lobes 72 to show that the porous silicon layer 12 of UHP 23A was more than 80% crystalline silicon in single crystal form; ie more than 80% of the Si atoms in the porous layer were unoxidised and on crystal lattice sites. In fact, it is believed that more than 90% of the Si atoms were unoxidised and on silicon lattice sites. It is believed that this porous silicon preserved the crystal structure of the original silicon wafer 10, since there is no other reasonable mechanism for such a structure to arise. This is a surprising result, because the supercritically dried specimen UHP 23A comprised quantum wires of 3 nm to 5 nm diameter in air. The interatomic spacing in silicon is 0.235 nm, so 3 nm to 5 nm diameter quantum wires have only 12 to 21 atoms across a diameter; of these at least the outermost atoms will not be on crystal lattice sites once they become oxidised. It is in fact surprising that the supercritically dried specimen UHP 23A was less than 10% oxidised, since it had been stored for one month between production and electron diffraction measurement.

[0024] In order to compare luminescent properties of porous silicon material produced in accordance with the invention with that produced by a prior art procedure, two further specimens, referred to as UHP 17 and UHP 26B respectively, were prepared. Specimen UHP 17 was produced as follows. A wafer of p⁺ silicon material with resistivity in the range $5 \times 10^{-3} \text{ ohm cm}$ to $15 \times 10^{-3} \text{ ohm cm}$ was anodized in 10% ethanoic HF solution at a current density of 50 mAcm⁻² for 3 minutes. This wafer

was then etched for 15 minutes by being left to soak in the same solution. It was subsequently rinsed in pure ethanol to remove etchant, and then dried in air. As a result of this processing, the wafer bore a porous silicon layer which had partly disintegrated by cracking and peeling. Detached flakes of the porous layer were imaged in a transmission electron microscope (TEM). The flakes proved to contain quantum wires with diameters in the range 4.5 nm to 6 nm. A porosity value can be quoted for this layer, but it would be of doubtful value because of the layer's partial disintegration.

[0025] A second wafer of p⁺ silicon material with resistivity in the range 15×10^{-3} ohm cm to 50×10^{-3} ohm cm was used to make specimen UHP 26B. The wafer was anodized for 5 minutes in 10% ethanoic HF solution at a current density of 50 mAcm⁻². It was then etched for 5 minutes by being left to soak in the same solution. Experience shows that the resulting porous silicon layer so produced on the wafer would craze and disintegrate substantially completely if dried in air. The original wafer was of higher resistivity than that used to make UHP 17, and increase in resistivity improves luminescence properties but also increases likelihood of disintegration.

[0026] Instead UHP 26B was dried by a supercritical drying process similar to that described earlier with reference to Figures 1 and 2. The wafer was soaked in ethanol to remove etchant from the pores of the porous silicon layer; it was then dried in a pressure vessel of 10 cm³ capacity by replacing the ethanol with liquid CO₂ at a temperature of 18°C and a pressure of 1500 psi (10.1 MPa).

[0027] The temperature was then raised to 40°C over a 15 minute time interval and flushed with supercritical CO₂ for 15 minutes. A one hour interval was employed for depressurization of specimen to UHP 26B to atmospheric pressure. After removal from the pressure vessel, this specimen exhibited no crazing, cracking or partial disintegration. It exhibited the same morphology as that described for specimen UHP 23A despite the relatively more rapid depressurization.

[0028] Specimens UHP 17 and UHP 26B were tested for photoluminescence properties by being subjected to irradiation with 0.1 watt cm⁻² of argon ion laser radiation of 458 nm wavelength. This was carried out in air at ambient temperature. Specimen UHP 17 had undergone storage in air at ambient temperature subsequent to formation and prior to irradiation. The photoluminescence spectra are shown in Figure 8, graphs (a) and (b) being those of Specimens UHP 17 and UHP 26B respectively. The ordinate axis is photoluminescence intensity (arbitrary units) and the abscissa axis is wavelength (nm). Graph (a) has been displaced vertically to avoid overlapping spectra; the graphs both go to zero at 550 nm (at which a relative shift has been introduced), and graph (a) has undergone a tenfold (x10) ordinate scale expansion or relative magnification compared to graph (b). This can be appreciated from the much greater noise level of graph (a) relative to that of graph (b).

[0029] The photoluminescence emission band of graph (a) is wider than that of graph (b). Moreover, graph (b) has a peak photoluminescence emission centred at about 757 nm, compared with about 778 nm for graph (a). Graph (b) is therefore blue-shifted slightly relative to graph (a), and has higher peak intensity having regard to the relative magnification of graph (a) previously mentioned. The integrated photoluminescence intensity (peak intensity multiplied by full width at half height) of graph (b) is six times that of graph (a). These differences are collectively consistent with specimen UHP 26B incorporating smaller quantum wires than specimen UHP 17, giving a higher degree of quantum confinement, and having higher quantum wire density. Calculations show that specimen UHP 26B exhibits a photoluminescence efficiency of greater than 0.1%. Furthermore, Figure 8 is evidence that supercritical drying does not merely preserve the luminescence properties of porous silicon, but also provides enhancement of those properties. The combination of specimen UHP 26B and the activating Argon ion laser constitutes a luminescent device.

[0030] An example of the invention, specimen UHP 23C cut from the same wafer as UHP 23A, was used to investigate the morphology of material of the invention. Transmission electron microscopy (TEM) was used to study specimen UHP 23C; this specimen proved to contain silicon quantum wires with diameters less than 4 nm, and it consisted of a three dimensional reticulated structure of silicon quantum wires at least 50% of which were less than 4 nm in diameter. At least 90% of the silicon in this structure was in the form of silicon quantum wires.

[0031] The invention provides inter alia an electrochemical process for producing porous crystalline silicon material supported by and attached to a bulk (ie non-porous) silicon substrate, the porous silicon being initially in a wetted state and dried by a supercritical drying process. The invention provides crystalline porous silicon with luminescence properties; the porous silicon is attached to and is an extension of the crystal structure of non-porous crystalline silicon material from which the porous silicon was produced by removal of silicon material. The porous silicon is a three dimensional branched network of quantum wires in which the luminescence properties arise from quantum confinement of charge carriers. Luminescence properties of porous silicon are improved by increase in quantum confinement, which requires reduction in quantum wire diameter and therefore increase in porosity. At least in p⁺ silicon, these properties are also improved by increased resistivity of the bulk silicon wafer used to produce the porous silicon material.

[0032] Porosity data quoted above was obtained for specimens UHP 23A and others by a gravimetric procedure described in International Application No. PCT/GB90/01901 previously mentioned. This procedure involves determining the weight of silicon lost in anodization and etching and calculating an average density for

the porous silicon assuming it retains its pre-anodization shape. The porous silicon density is then divided by the density of bulk silicon, and the result is subtracted from unity to provide a porosity figure. The validity of this depends on the porous silicon preserving its shape. If there is shrinkage during drying, the actual porosity will be lower than that indicated by gravimetric data.

[0033] Ellipsometric spectroscopy was employed to determine the thickness of the air dried comparison specimen UHP 23 and the supercritically dried specimen UHP 23A. The results are shown in Figure 9. Ellipsometry is a known technique for optically characterising surfaces and surface films or layers. It involves determining the amplitude ratio ($\tan \psi$) and phase difference ($\cos \Delta$) of light beams reflected from a surface under test and p-polarized and s-polarised respectively in relation to that surface. This is carried out over a range of wavelengths. Subsequently the data is fitted to a theoretical model, in which the surface layer's pseudo-refractive indices and thickness are parameters. Porosity is obtainable from comparison with the optical properties of non-porous (bulk) crystalline silicon. See for example Pickering et al., *Applied Surface Science* 63 (1993) pages 22-26.

[0034] In Figure 9, the ellipsometric amplitude ratio ψ (Psi) in degrees is plotted against photon energy (eV) for UHP 23 (air dried) and UHP 23A (supercritically dried). This is shown in each case both for measured ellipsometry data and for calculations from a theoretical model forming a best fit to such data. The upper right of the drawing gives a key to the graphs shown. The theoretical model employed is a multilayer effective medium model of a kind known in ellipsometry. Graphs 90 (measured data) and 92 (theoretical model) were obtained from supercritically dried specimen UHP 23A shown in Figures 4 and 6. The oscillatory behaviour is due to interference fringes, and indicates good optical quality. The theoretical model is a reasonable fit; it overestimates fringe amplitude, probably due to porosity gradient and/or non-ideal interfaces. It indicates a thickness of the porous silicon layer of $4.98 \pm 0.05 \mu\text{m}$, together with a porosity (percentage void) varying from 97% (surface remote from substrate) to 92% (adjacent to substrate). This is consistent with etching decreasing with penetration depth, which is normal. UHP 23A therefore has a thickness of about $5 \mu\text{m}$ and an average porosity of about 95% determined ellipsometrically. The porosity figure of 97% corresponds to the outer or upper $0.25 \mu\text{m}$ thickness of the porous silicon 62 in Figure 6. This porosity is consistent with an average density of 0.09 g/cm^3 and a refractive index less than 1.10.

[0035] Graphs 94 (measured data) and 96 (theoretical model) were obtained for the air dried comparison specimen UHP 23. They do not show interference fringes, indicating that coherency with the substrate has been lost and that optical quality is poor. The measured data can be fitted with an average porosity of 83% assuming a free standing porous layer; this is consistent

with cross-sectional SEM results (see Figure 5) showing that the porous layer had at least partially lifted off (become detached) from the bulk silicon substrate. The data also indicated a reverse or negative porosity gradient of 80% at the outer surfaces increasing to 85% adjacent to the substrate; this is consistent with collapse of at least part of the porous structure.

[0036] The difference between the ellipsometric porosity results for UHP 23 and UHP 23A indicates that the former experienced a shrinkage over 10% relative to the latter. Such shrinkage can be inferred from Figure 5, in which the porous silicon material contains voids 54 and has a concave upper surface consistent with shrinking during drying. Figure 6 however demonstrates that such shrinkage is not detectable in supercritically dried specimen UHP 23A. From Figure 6 it can be seen that the thickness of specimen UHP 23A is constant to within 5% over a distance of $20 \mu\text{m}$ measured parallel to the surface of the silicon substrate 64. This thickness is $4.0 \pm 0.2 \mu\text{m}$. Over the whole of specimen UHP 23A (area 2 cm^2), porous silicon thickness variation was less than 10%. This compares with a variation in thickness of air dried specimen UHP 23 which approaches 100%; ie the thickness varies between about $4 \mu\text{m}$ and less than $0.1 \mu\text{m}$ due to voids 56 in the porous silicon material of this specimen. The voids 56 extend virtually down to the substrate 54, and the near 100% thickness variation occurs over distances of only a few μm between adjacent voids 56.

[0037] Supercritical drying is known per se for the production of aerogels, these being structures which are over 90% porous and the pores are air filled. Tewari et al. describe the production of transparent silica aerogels in *Materials Letters*, Vol. 3, No. 9, 10 pages 363 to 367, July 1985. The silica aerogel is produced from a solution by a sol-gel process; the process involves hydrolysis and polycondensation of silicon alkoxides in alcohol, which produces an alcogel (ie alcohol-filled pores). The aerogel is produced by replacing the alcohol in the pores by air. This is done by supercritical drying. The silica aerogels are non-crystalline and are free standing; ie there is no supporting substrate. They are insulators not semiconductors, and Tewari et al. do not disclose luminescence properties.

[0038] Supercritical drying for the production of silica aerogels is also disclosed by Rangarajan and Lira, *J. Supercritical Fluids*, Vol 4, No. 1, pages 1 to 7, 1991. The original work in this field was carried out by Kistler in 1932, and is reported in *J. Phys. Chem* 1932, 36, 52. Published Japanese Patent Application Number JP 890266463 describes a method of drying semiconductor substrates using supercritical drying techniques to give increased yield through the avoidance of attaching foreign matter to the substrate.

[0039] Semiconductor processing is a high technology field with considerable research and development activity in many countries. Semiconductor processing is directed to layers or strata supported by bulk (non-po-

rous) wafer substrate. Layers grown epitaxially on a substrate are extensions of the substrate's crystal structure, ie a substrate and semiconductor layers thereon from a single crystal. The layers are of microscopic thickness, typically a few μm in thickness or less down to a fraction of a μm . A porous silicon "layer" is a skeleton structure formed by etching to remove material from a silicon wafer to which the skeleton is attached. It is referred to in this specification, as an aerocrystal or aerocrystal network, and is an extension of a non-porous crystalline substrate. Pores in the porous silicon terminate at the wafer. Aerogels are formed by condensation from solution, not from an original non-porous solid phase material. An aerogel therefore has no substrate of such original material, and all its surfaces are porous. Aerogels are amorphous, ie non-crystalline; they are of macroscopic dimensions, mm or cm in thickness, as opposed to μm thicknesses for semiconductor layers.

[0040] In a textbook, "Chemical Processing of Advanced Materials", pp 19 onwards, Ed. Hench and West, 1992, John Wiley and Sons, Hrubesh et al. describe the production of very high porosity silica aerogels. They observe that such aerogels are hydrophobic if produced by direct extraction of solvent, and are stable in atmosphere. However, silica aerogels are hydrophilic when produced by first exchanging the solvent with carbon dioxide and supercritically drying. They shrink badly when exposed to air. This has surprisingly been found not to be the case for supercritically dried porous silicon. It is also surprising that the high pressures involved in supercritical drying have not produced any serious etching effects associated with the solvent being displaced from porous silicon. In this regard it is observed that alcohols in porous silicon are associated with heat evolution indicating etching. This is reported by Canham and Groszek in J. Appl. Phys. Vol 72 (4), pages 1558-1564, 15 August 1992.

[0041] The supercritical drying process may also be used to fabricate thick luminescent porous silicon layers which are of the order of 200 μm in thickness. Such layers having a porosity of greater than 70% averaged over the depth of the porous layer have been produced and their luminescence properties characterized.

[0042] Referring now to Figure 10, there is shown in graphical form a plot of luminescence intensity in arbitrary units versus depth for a cross-section of a thick luminescent porous silicon layer. The thick luminescent porous silicon layer was fabricated by the following method. A wafer of silicon material heavily doped with arsenic to form a n^+ wafer, with a resistivity in the range $5 \times 10^{-3} \text{ ohm cm}$ to $10 \times 10^{-3} \text{ ohm cm}$ was used to produce the very thick porous layer. The wafer was anodized in a 20% ethanoic HF solution, comprising a 1:1 ethanol:40 wt% HF solution, at 50 mAcm^{-2} for 90 minutes. The wafer was then subjected to a chemical etch in the same solution for 2 hours. Following the etching process, the wafer was removed from the HF solution and immersed in isopropyl alcohol (IPA) whilst still wet.

The wafer was kept immersed in the IPA for 18 hours prior to commencement of the supercritical drying process. The supercritical drying was carried out in a similar manner to that described earlier in relation to Figure 2 except that that IPA rather than ethanol was used as the intermediate solvent. Segments of the wafer were dried in a 50 cm^3 pressure vessel which was flushed with liquid CO_2 at a temperature of 18°C and a pressure of 10.1 MPa with a flow rate of $5 \text{ cm}^3 \text{ min}^{-1}$ for 80 minutes to remove most of the IPA. The temperature was then raised at a rate of 2°C min^{-1} to 40°C and the sample flushed with supercritical CO_2 for 50 minutes. The pressure vessel was then de-pressurized at 40°C over a period of 10 minutes. The wafer segment had a porous silicon layer approximately 200 μm thick with a porosity of greater than 70% throughout the entire depth of the layer. The porosity was measured using a gravimetric technique. After supercritical drying, the wafer segment was stored in ambient air for 47 days prior to luminescence measurements being performed.

[0043] Figure 10 was obtained using measurement techniques as described by Beale et al. in Materials Research Society Symposium Proceedings, Volume 283, 1993, pages 377-382. A cross-section of the porous silicon layer was illuminated using a 442 nm HeCd laser and the intensity of the resulting visible photoluminescence was measured as a function of position across the porous silicon layer. The extent of the porous silicon region is indicated by an arrow 100, with the porous silicon region having top and bottom surfaces corresponding to dotted lines 102 and 104 respectively. Figure 10 shows that photoluminescence was achieved throughout the porous silicon layer, with the luminescence intensity decreasing with increasing depth. The efficiency of the luminescence was measured for the top porous silicon surface, i.e. the surface furthest from the silicon wafer, corresponding to dotted line 102 at a depth of 0 μm in Figure 10. The measured external power efficiency was 0.54%. Using this value for luminescence efficiency at the porous silicon top surface, it is possible to calibrate Figure 10. The luminescence efficiency falls below 0.3% at a depth indicated by a chain line 105, indicating that the porous silicon has a luminescence efficiency of more than 0.3% over more than 100 μm , or 50% of the porous silicon thickness. The luminescence efficiency falls below 0.1% at a depth indicated by a chain line 106, indicating that the porous silicon has a luminescence efficiency of greater than 0.1% over more than 160 μm , or 80% of the porous silicon thickness. The porous silicon layer therefore has more than 80% of its thickness exhibiting good luminescence properties. The combination of the thick porous silicon layer and the illuminating laser comprises a luminescent device. The wafer was examined in an SEM and was found to have good structural integrity, with no evidence of cracking of the porous silicon layer being observed in a sample measuring 2 cm by 4 cm.

[0044] Thick photoluminescent porous silicon with a

thickness of $32 \pm 5 \mu\text{m}$ and good structural integrity, showing no evidence of cracking under scanning electron microscopy has also been fabricated from lightly doped p-type (p⁻) silicon. A cz p⁻ silicon wafer of resistivity in the range 1-3 ohm cm was anodized in a 20% ethanoic HF solution for 90 minutes at 20 mAcm⁻². The anodized wafer was then immersed in IPA whilst still wet. The wafer was then dried supercritically in the same manner as for the 200 μm thick sample described previously. Visible photoluminescence was observed across the entire porous silicon layer under cross-sectional flood illumination with 442 nm radiation. When illuminated with 325 nm ultraviolet radiation, the porous silicon luminesced with a peak wavelength of 575 nm. The efficiency of the photoluminescence was measured to be more than 1% extending over a thickness of greater than 20 μm .

[0045] Thick porous silicon layers have been observed previously. N. Ookubo et al. in Material Science and Engineering B20 (1993) pp 324 to 327 reported the production of porous silicon films having a thickness of up to 94 μm . However, the films produced by Ookubo et al. have a layered structure, with only a top layer of thickness 6-8 μm being described as visibly photoluminescent. The top surface of the Ookubo films are shown as being cracked into cells with a lateral dimension of approximately 10 μm . In another paper by Ookubo in J. Appl. Phys 74 (10), 15 November 1993, pp 6375 to 6382, describing a two-layer structure of approximately 8 μm in thickness, the layer structure is attributed to the process of removing the electrolyte after anodization. Grivickas et al. in their paper referenced earlier also observed a layered structure to their porous silicon films under scanning electron microscopy. These films were up to 50 μm thick and are described as being weakly photoluminescent but again showed cracking. It seems probable that the layered structure is a result of the top layer having higher porosity which collapses when the sample is dried. It is desirable to be able to form luminescent porous silicon layers of thickness greater than 10 μm which do not have a layered structure. It is also desirable to form luminescent porous silicon layers of thickness greater than 10 μm which do not exhibit cracking. Neither the 200 μm thick n⁺ porous silicon layer nor the 32 μm thick p⁻ porous silicon layer exhibited a layer structure under cross-sectional scanning electron microscopy. Also, neither the 200 μm thick n⁺ porous silicon layer nor the 32 μm thick p⁻ porous silicon layer exhibited voids, crazing or peeling during examination by scanning electron microscopy at a magnification of 7,000.

[0046] Whereas the invention is particularly relevant to porous silicon, it is also relevant to other porous semiconductor materials such as porous gallium arsenide.

Claims

1. Porous semiconductor material (12) which is at least partly crystalline, **characterised in that** the semiconductor material has a porosity in excess of 90% determined gravimetrically and **in that** the porous semiconductor material has one or more of the following properties:
 - there are substantially no voids (56), crazing and peeling discernable in the semiconductor material by scanning electron microscopic analysis at a magnification of 7,000;
 - the semiconducting material has a crack density of less than 10^8 cm^{-2} ; and
 - the semiconductor material is free of cracks greater than 0.1 μm in width.
2. Material according to Claim 1, **characterised in that** the porous semiconductor material (12) is porous silicon material.
3. Material according to Claim 2, **characterised in that** the material is at least 80% crystalline.
4. Material according to Claim 3, **characterised in that** the material has a thickness which is constant to within 10%.
5. Material according to Claim 4, **characterised in that** the material is connected to a non-porous silicon substrate.
6. Material according to Claim 2, **characterised in that** the material is connected to a non-porous silicon substrate.
7. Material according to Claim 2, **characterised in that** the material contains silicon quantum wires with diameters less than 4nm.
8. Material according to Claim 7, **characterised in that** at least 90% by volume of the material consists of a reticulated structure of silicon quantum wires and at least 50% of the said wires have diameters less than 4 nm.
9. Material according to Claim 8, **characterised in that** the material is at least 80% crystalline.
10. Material according to Claim 2, **characterised in that** the material is in the form of an aerocrystal connected to a non-porous crystalline silicon substrate (64) of like crystal structure.
11. Material according to any one of Claims 2 to 10,

- characterised in that** the material is activatable to produce visible luminescence.
12. Material according to Claim 1, **characterised in that** the material is in the form of an aerocrystal connected to a non-porous crystalline substrate (64) of like semiconductor material.
 13. Porous semiconductor material (12) according to Claim 1 **characterised in that** in voids (56), crazing and peeling are substantially indiscernible by scanning electron microscopy at a magnification of 7,000. of an area of at least $20\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$.
 14. A luminescent device incorporating porous semiconductor (12) material according to Claim 1 which is activatable to produce visible luminescence, the device also incorporating means for exciting luminescence from the porous semiconductor material (12).
 15. A device according to Claim 14, **characterised in that** the porous semiconductor is porous silicon material.
 16. A device according to Claim 15, **characterised in that** the porous silicon material is at least 80% crystalline.
 17. A device according to Claim 16, **characterised in that** the porous silicon material has a thickness which is constant to within 10%.
 18. A device according to Claim 15, **characterised in that** the porous silicon material contains silicon quantum wires with diameters less than 4 nm.
 19. A device according to Claim 18, **characterised in that** at least 90% by volume of the porous silicon material consists of a reticulated structure of silicon quantum wires and at least 50% of the said wires have diameters less than 4 nm.
 20. A device according to any one of Claims 15 to 19, **characterised in that** the porous silicon material is connected to a non-porous crystalline silicon substrate (64).
 21. A luminescent device according to Claim 14, **characterised in that** voids (56), crazing and peeling are substantially indiscernible by scanning electron microscopy at a magnification of 7,000 of an area of at least $20\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$.
 22. A method of making porous semiconductor material incorporating the step of producing porous semiconductor material (12) which is liquid-wetted and at least partly crystalline, **characterised in that** the method further incorporates the step of drying the porous semiconductor material (12) by a supercritical drying process.
 23. A method according to Claim 22, **characterised in that** the step of producing porous semiconductor material which is liquid-wetted and at least partly crystalline involves producing porous semiconductor material which is porous silicon material with a porosity in excess of 90% determined gravimetrically.
 24. A method according to Claim 23, **characterised in that** the step of producing porous semiconductor material which is liquid-wetted and at least partly crystalline involves an electrochemical process to produce porous silicon material.
 25. A method according to Claim 24, **characterised in that** after drying the porous silicon material has at least 80% crystallinity, porosity in excess of 90% determined gravimetrically, and indiscernibility of voids (56), crazing and peeling by scanning electron microscopy at a magnification of 7,000.
 26. A method according to Claim 25, **characterized in that** after drying at least 90% by volume of the porous silicon material consists of a reticulated structure of silicon quantum wires and at least 50% of the said wires have diameters less than 4 nm.
 27. A method according to Claim 24, **characterized in that** the step of producing porous semiconductor material which is liquid-wetted and at least partly crystalline involves an anodization/etching process to produce porous silicon material connected to a substantially non-porous crystalline silicon substrate (10,64).
 28. A method according to Claim 27, **characterized in that** the anodization/etching process comprises anodizing a substantially non-porous crystalline silicon substrate (10,64) to produce porous and at least partly crystalline silicon material connected thereto, and etching the porous silicon material to increase its porosity, etching being terminated with the porous silicon material in a liquid-wetted state for drying by the supercritical drying process.
 29. A method according to any one of Claims 22 to 28, **characterized in that** the supercritical drying process involves replacement of liquid in the pores of the porous silicon by liquid CO_2 and a subsequent change of the CO_2 phase from liquid to gas.
 30. A method of making porous semiconductor material according to Claim 22, **characterized in that** after drying the porous silicon is activatable to produce

visible luminescence.

31. A method according to Claim 30, **characterized in that** the porous semiconductor material is porous silicon material.
32. A method according to Claim 31, **characterized in that** the porous semiconductor material has a sheet thickness greater than 10 µm.
33. A method according to Claim 32, **characterised in that** the material has a sheet thickness greater than 100 µm.
34. A method according to Claim 32, **characterised in that** the material has a sheet thickness in the range 20 µm to 200 µm.

Patentansprüche

1. Poröses Halbleitermaterial (12), das zumindest teilweise kristallin ist, **dadurch gekennzeichnet, daß** das Halbleitermaterial eine gravimetrisch bestimmte Porosität über 90 % aufweist und dadurch, daß das poröse Halbleitermaterial eine oder mehrere der folgenden Eigenschaften aufweist:
 - in dem Halbleitermaterial sind bei einer Vergrößerung von 7000 in einem Rasterelektronenmikroskop im wesentlichen keine Leerräume (56), Haarrisse und Ablösungen erkennbar;
 - das Halbleitermaterial weist eine Dichte der Risse unter 10^8 cm^{-2} auf; und
 - das Halbleitermaterial weist keine Risse auf, die breiter als 0,1 µm sind.
2. Material nach Anspruch 1, **dadurch gekennzeichnet, daß** das poröse Halbleitermaterial (12) ein poröses Siliciummaterial ist.
3. Material nach Anspruch 2, **dadurch gekennzeichnet, daß** das Material zumindest zu 80 % kristallin ist.
4. Material nach Anspruch 3, **dadurch gekennzeichnet, daß** die Dicke des Materials innerhalb von 10 % konstant ist.
5. Material nach Anspruch 4, **dadurch gekennzeichnet, daß** das Material mit einem nichtporösen Siliciumsubstrat verbunden ist.
6. Material nach Anspruch 2, **dadurch gekennzeichnet, daß** das Material mit einem nichtporösen Siliciumsubstrat verbunden ist.
7. Material nach Anspruch 2, **dadurch gekennzeichnet,**

net, daß das Material Siliciumquantendrähte mit einem Durchmesser von weniger als 4 nm aufweist.

8. Material nach Anspruch 7, **dadurch gekennzeichnet, daß** mindestens 90 Vol-% des Materials aus einer vernetzten Struktur von Siliciumquantendrähten besteht und mindestens 50 % der Drähte einen Durchmesser unter 4 nm haben.
9. Material nach Anspruch 8, **dadurch gekennzeichnet, daß** mindestens 80 % des Materials kristallin sind.
10. Material nach Anspruch 2, **dadurch gekennzeichnet, daß** das Material in Form eines Aerokristalls vorliegt, der mit einem nichtporösen kristallinen Siliciumsubstrat (64) der gleichen Kristallstruktur verbunden ist.
11. Material nach einem der Ansprüche 2 bis 10, **dadurch gekennzeichnet, daß** das Material zur Lumineszenz im sichtbaren Bereich anregbar ist.
12. Material nach Anspruch 1, **dadurch gekennzeichnet, daß** das Material in Form eines Aerokristalls vorliegt, der mit einem nichtporösen kristallinen Substrat (64) des gleichen Halbleitermaterials verbunden ist.
13. Poröses Halbleitermaterial (12) nach Anspruch 1, **dadurch gekennzeichnet, daß** über eine Fläche von mindestens 20 µm x 10 µm bei einer Vergrößerung von 7000 in einem Rasterelektronenmikroskop im wesentlichen keine Leerräume (56), Haarrisse und Ablösungen erkennbar sind.
14. Lumineszierende Vorrichtung, die ein poröses Halbleitermaterial (12) nach Anspruch 1 enthält, das zur Lumineszenz im sichtbaren Bereich anregbar ist, wobei die Vorrichtung auch Einrichtungen enthält, um die Lumineszenz in dem porösen Halbleitermaterial (12) anzuregen.
15. Vorrichtung nach Anspruch 14, **dadurch gekennzeichnet, daß** es sich bei dem porösen Halbleiter um poröses Silicium handelt.
16. Vorrichtung nach Anspruch 15, **dadurch gekennzeichnet, daß** das poröse Siliciummaterial zumindest zu 80 % kristallin ist.
17. Vorrichtung nach Anspruch 16, **dadurch gekennzeichnet, daß** die Dicke des porösen Siliciums innerhalb von 10 % konstant ist.
18. Vorrichtung nach Anspruch 15, **dadurch gekennzeichnet, daß** das poröse Siliciummaterial Quantendrähte mit einem Durchmesser unter 4 nm ent-

hält.

19. Vorrichtung nach Anspruch 18, **dadurch gekennzeichnet, daß** mindestens 90 Vol-% des porösen Siliciummaterials aus einer vernetzten Struktur von Siliciumquantendrähten bestehen und mindestens 50 % der Drähte einen Durchmesser unter 4 nm aufweisen. 5
20. Vorrichtung nach einem der Ansprüche 15 bis 19, **dadurch gekennzeichnet, daß** das poröse Siliciummaterial mit einem nichtporösen kristallinen Siliciumsubstrat (64) verbunden ist. 10
21. Lumineszierende Vorrichtung nach Anspruch 14, **dadurch gekennzeichnet, daß** über eine Fläche von mindestens 20 µm x 10 µm bei einer Vergrößerung von 7000 in einem Rasterelektronenmikroskop im wesentlichen keine Leerräume (56), Haarrisse und Ablösungen erkennbar sind. 15
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22. Verfahren zur Herstellung porösen Halbleitermaterials mit einem Schritt zur Herstellung porösen Halbleitermaterials (12), das flüssigkeitsbenetzt und zumindest teilweise kristallin ist, **dadurch gekennzeichnet, daß** das Verfahren weiterhin einen Schritt zum Trocknen des porösen Halbleitermaterials (12) in einem überkritischen Trockenprozeß umfaßt. 25
30
23. Verfahren nach Anspruch 22, **dadurch gekennzeichnet, daß** der Schritt zur Herstellung porösen Halbleitermaterials, das flüssigkeitsbenetzt und zumindest teilweise kristallin ist, die Herstellung porösen Halbleitermaterials umfaßt, bei dem es sich um poröses Siliciummaterial mit einer gravimetrisch bestimmten Porosität über 90 % handelt. 35
24. Verfahren nach Anspruch 23, **dadurch gekennzeichnet, daß** der Schritt zur Herstellung porösen Halbleitermaterials, das flüssigkeitsbenetzt und zumindest teilweise kristallin ist, einen elektrochemischen Prozeß zur Herstellung porösen Siliciummaterials umfaßt. 40
25. Verfahren nach Anspruch 24, **dadurch gekennzeichnet, daß** das poröse Siliciummaterial nach dem Trocknen eine Kristallinität von mindestens 80 % und eine gravimetrisch bestimmte Porosität über 90 % aufweist und bei einer Vergrößerung von 7000 im Rasterelektronenmikroskop keine Leerräume (56), Haarrisse und Ablösungen erkennbar sind. 45
50
26. Verfahren nach Anspruch 25, **dadurch gekennzeichnet, daß** nach dem Trocknen mindestens 90 Vol-% des porösen Siliciummaterials aus einer vernetzten Struktur von Siliciumquantendrähten bestehen und mindestens 50 % der Drähte einen

Durchmesser von unter 4 nm aufweisen.

27. Verfahren nach Anspruch 24, **dadurch gekennzeichnet, daß** der Schritt zur Herstellung porösen Halbleitermaterials, das flüssigkeitsbenetzt und zumindest teilweise kristallin ist, ein Anodisier/Ätzverfahren zur Herstellung porösen Siliciummaterials umfaßt, das mit einem im wesentlichen nichtporösen kristallinen Siliciumsubstrat (10, 64) verbunden ist.
28. Verfahren nach Anspruch 27, **dadurch gekennzeichnet, daß** das Anodisier/Ätzverfahren das Anodisieren eines im wesentlichen nichtporösen kristallinen Siliciumsubstrats (10, 64) zur Herstellung eines damit verbundenen porösen und zumindest teilweise kristallinen Siliciummaterials und ein Ätzen des porösen Siliciummaterials zur Erhöhung seiner Porosität umfaßt, wobei das poröse Siliciummaterial vor dem Trocknen mit einem überkritischen Trockenverfahren nach dem Ätzen in einem flüssigkeitsbenetzten Zustand vorliegt.
29. Verfahren nach einem der Ansprüche 22 bis 28, **dadurch gekennzeichnet, daß** das überkritische Trockenverfahren ein Ersetzen der Flüssigkeit in den Poren des porösen Siliciums durch flüssiges CO₂ mit einem anschließenden Übergang der CO₂-Phase von einer flüssigen in eine gasförmige Phase umfaßt. 30
30. Verfahren zur Herstellung porösen Halbleitermaterials nach Anspruch 22, **dadurch gekennzeichnet, daß** das poröse Silicium nach dem Trocknen zur Lumineszenz im sichtbaren Bereich anregbar ist. 35
31. Verfahren nach Anspruch 30, **dadurch gekennzeichnet, daß** es sich bei dem porösen Halbleitermaterial um poröses Siliciummaterial handelt.
32. Verfahren nach Anspruch 31, **dadurch gekennzeichnet, daß** das poröse Halbleitermaterial eine Schichtdicke von mehr als 10 µm aufweist.
33. Verfahren nach Anspruch 32, **dadurch gekennzeichnet, daß** das Material eine Schichtdicke über 100 µm aufweist. 45
34. Verfahren nach Anspruch 32, **dadurch gekennzeichnet, daß** das Material eine Schichtdicke im Bereich von 20 µm bis 200 µm aufweist. 50

Revendications

1. Matériau semiconducteur poreux (12) qui est au moins partiellement cristallin, **caractérisé en ce que** le matériau semiconducteur a une porosité su-

périeure à 90 % déterminée par gravimétrie et en ce que le matériau semiconducteur poreux a l'une au moins des propriétés suivantes :

- il n'existe pratiquement pas de vide (56), fissuration et délamination visibles dans le matériau semiconducteur au travers d'une analyse par microscope à balayage électronique à un grossissement de 7000 fois ;
le matériau semiconducteur a une densité de fissuration inférieure à 10^8 cm^{-2} ; et
le matériau semiconducteur est exempt de fissurations dont la largeur est supérieure à $0,1 \mu\text{m}$.
2. Matériau selon la revendication 1, **caractérisé en ce que** le matériau semiconducteur poreux (12) est du silicone poreux.
3. Matériau selon la revendication 2, **caractérisé en ce que** le matériau est cristallin à au moins 80 %.
4. Matériau selon la revendication 3, **caractérisé en ce que** l'épaisseur du matériau est constante à 10 % près.
5. Matériau selon la revendication 4, **caractérisé en ce que** le matériau est joint à un substrat de silicone non poreux.
6. Matériau selon la revendication 2, **caractérisé en ce que** le matériau est joint à un substrat de silicone non poreux.
7. Matériau selon la revendication 2, **caractérisé en ce que** le matériau contient des fils quantiques de silicone dont le diamètre est inférieur à 4 nm.
8. Matériau selon la revendication 7, **caractérisé en ce qu'**au moins 90 % en volume du matériau sont composés d'une structure réticulée de fils quantiques de silicone et au moins 50 % desdits fils ont des diamètres inférieurs à 4 nm.
9. Matériau selon la revendication 8, **caractérisé en ce que** le matériau est cristallin à au moins 80 %.
10. Matériau selon la revendication 2, **caractérisé en ce que** le matériau se présente sous la forme d'un aérocristal joint à un substrat de silicone cristallin non poreux (64) de même structure cristalline.
11. Matériau selon l'une quelconque des revendications 2 à 10, **caractérisé en ce que** le matériau peut être activé pour produire une luminescence visible.
12. Matériau selon la revendication 1, **caractérisé en ce que** le matériau se présente sous la forme d'un

aérocristal joint à un substrat cristallin non poreux (64) de même matériau semiconducteur.

13. Matériau semiconducteur poreux (12) selon la revendication 1, **caractérisé en ce que** dans les vides (56), les fissurations et la délamination sont pratiquement invisibles au microscope à balayage électronique à un grossissement de 7000 fois sur une surface d'au moins $20 \mu\text{m} \times 10 \mu\text{m}$.
14. Dispositif luminescent qui intègre des matériaux semiconducteurs poreux (12) selon la revendication 1, qui peut être activé pour produire une luminescence visible, le dispositif intégrant également des moyens d'exciter la luminescence du matériau semiconducteur poreux (12).
15. Dispositif selon la revendication 14, **caractérisé en ce que** le semiconducteur poreux est du silicone poreux.
16. Dispositif selon la revendication 15, **caractérisé en ce que** le silicone poreux est cristallin à au moins 80 %.
17. Dispositif selon la revendication 16, **caractérisé en ce que** le silicone poreux est d'épaisseur constante dans des limites de 10 %.
18. Dispositif selon la revendication 15, **caractérisé en ce que** le silicone poreux contient des fils quantiques de silicone dont le diamètre est inférieur à 4 nm.
19. Dispositif selon la revendication 18, **caractérisé en ce qu'**au moins 90 % en volume du silicone poreux sont composés d'une structure réticulée de fils quantiques de silicone et au moins 50 % desdits fils ont des diamètres inférieurs à 4 nm.
20. Dispositif selon les revendications 15 à 19, **caractérisé en ce que** le silicone poreux est joint à un substrat de silicone cristallin non poreux (64).
21. Dispositif luminescent selon la revendication 14, **caractérisé en ce que** les vides (56), la fissuration et la délamination sont pratiquement invisibles par microscope à balayage électronique à un grossissement de 7000 fois d'une surface d'au moins $20 \mu\text{m} \times 10 \mu\text{m}$.
22. Procédé de fabrication de matériau semiconducteur poreux qui intègre la phase de production de matériau semiconducteur poreux (12) qui est humidifié et au moins partiellement cristallin, **caractérisée en ce que** le procédé comprend également la phase de séchage du matériau semiconducteur poreux (12) par un procédé de séchage supercritique.

23. Procédé selon la revendication 22, **caractérisé en ce que** la phase de production du matériau semi-conducteur poreux qui est humidifié et au moins partiellement cristallin implique la production de matériau semiconducteur poreux qui est du silicone poreux avec une porosité supérieure à 90 % déterminée par gravimétrie.
24. Procédé selon la revendication 23, **caractérisé en ce que** la phase de production du matériau semi-conducteur poreux qui est humidifié et au moins partiellement cristallin implique un processus électrochimique pour produire le silicone poreux.
25. Procédé selon la revendication 24, **caractérisé en ce qu'**après séchage, le silicone poreux est cristallin à au moins 80 %, a une porosité de plus de 90 % déterminée par gravimétrie, et qu'il n'est pas possible de discerner de vides (56), de fissurations et de délamination par microscope à balayage électronique à un grossissement de 7000 fois.
26. Procédé selon la revendication 25, **caractérisé en ce qu'**après séchage, au moins 90 % du silicone poreux sont composés d'une structure réticulée de fils quantiques de silicone et au moins 50 % desdits fils ont un diamètre inférieur à 4 nm.
27. Procédé selon la revendication 24, **caractérisé en ce que** la phase de production de matériau semi-conducteur poreux qui est humidifié et au moins partiellement cristallin implique un processus d'anodisation et/ou dérochage pour produire du silicone poreux joint à un substrat de silicone cristallin substantiellement non poreux (10, 64).
28. Procédé selon la revendication 27, **caractérisé en ce que** le processus d'anodisation et/ou dérochage comprend l'anodisation d'un substrat de silicone cristallin substantiellement non poreux (10, 64) pour produire un matériau silicone poreux et au moins partiellement cristallin joint, et le dérochage du matériau silicone poreux pour augmenter sa porosité, le dérochage s'achevant quand le matériau silicone poreux est en état humide en vue de son séchage par le procédé de séchage supercritique.
29. Procédé selon l'une des revendications 22 à 28, **caractérisé en ce que** le procédé de séchage supercritique implique le remplacement du liquide dans les pores du silicone poreux par du CO₂ liquide et le changement successif de la phase du CO₂ de l'état liquide à l'état gazeux.
30. Procédé de fabrication de matériau semiconducteur poreux selon la revendication 22, **caractérisé en ce qu'**après le séchage, le silicone poreux peut être activé pour produire une luminescence visible.
31. Procédé selon la revendication 30, **caractérisé en ce que** le matériau semiconducteur poreux est du silicone poreux.
32. Procédé selon la revendication 31, **caractérisé en ce que** le matériau semiconducteur poreux a une épaisseur supérieure à 10 µm.
33. Procédé selon la revendication 32, **caractérisé en ce que** l'épaisseur du matériau est supérieure à 100 µm.
34. Procédé selon la revendication 33, **caractérisé en ce que** l'épaisseur du matériau est comprise entre 20 µm et 200 µm.

Fig.1.

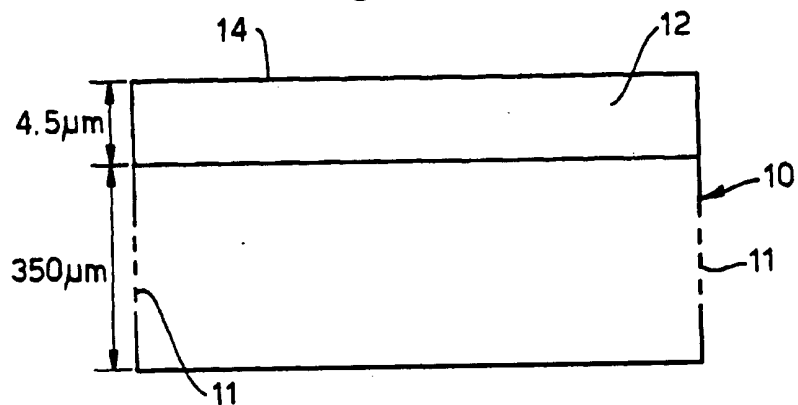


Fig.2.

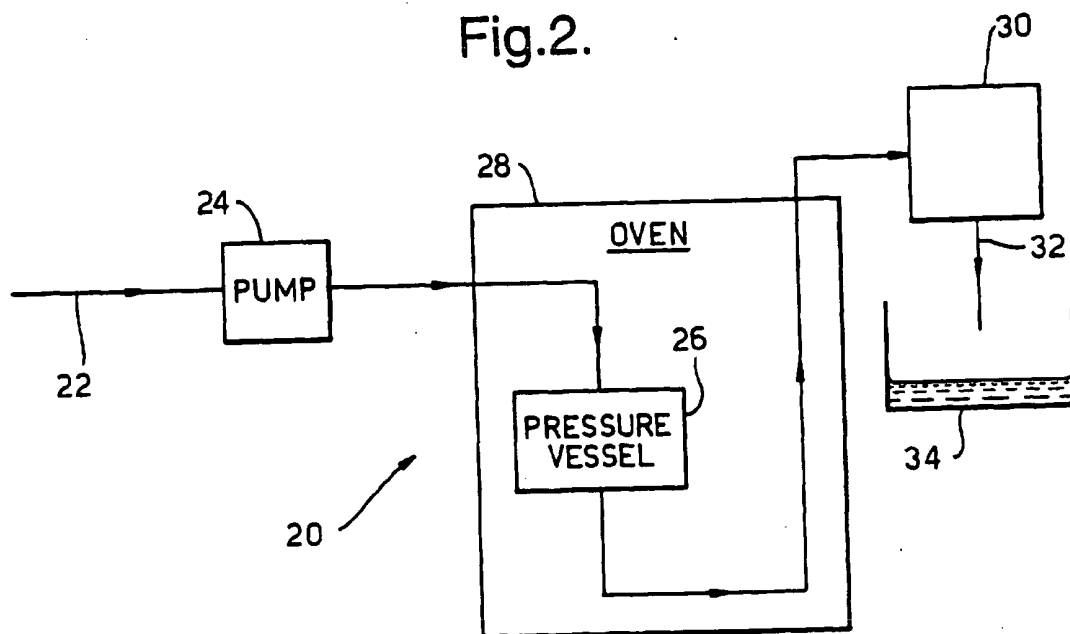


Fig.3.

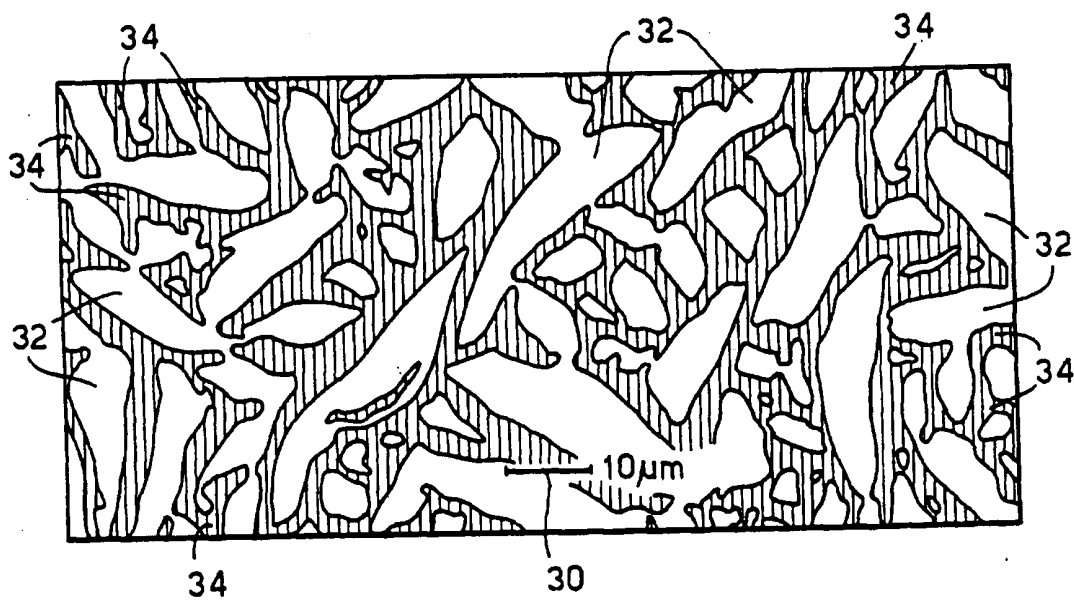


Fig.4.

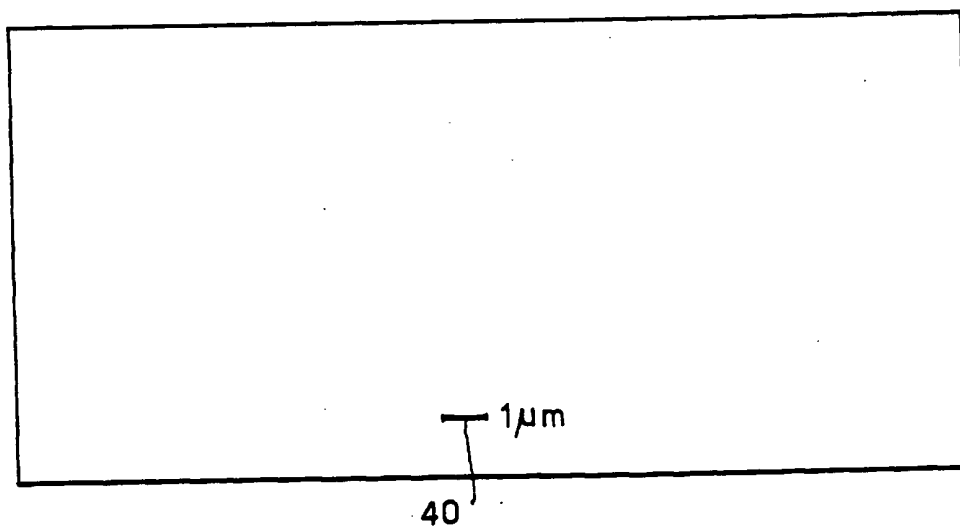


Fig.5.

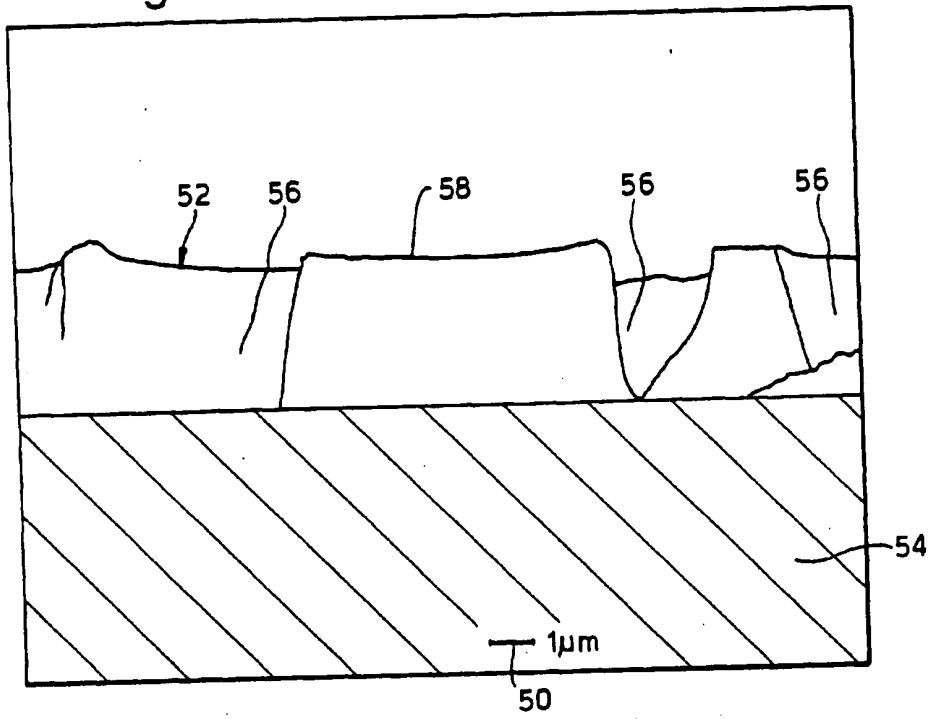


Fig.6.

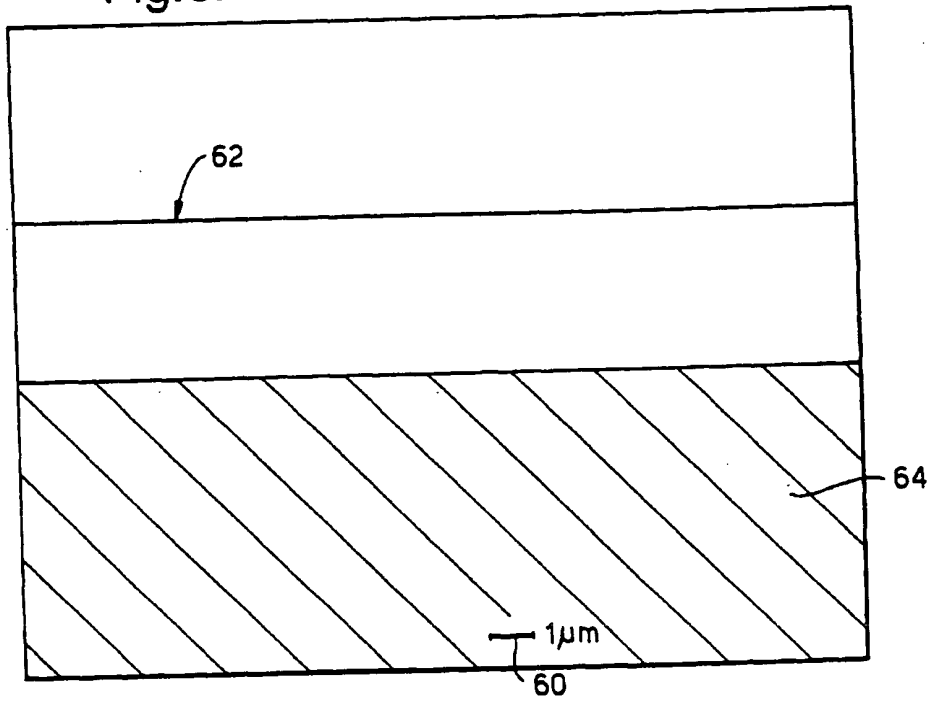


Fig.7.

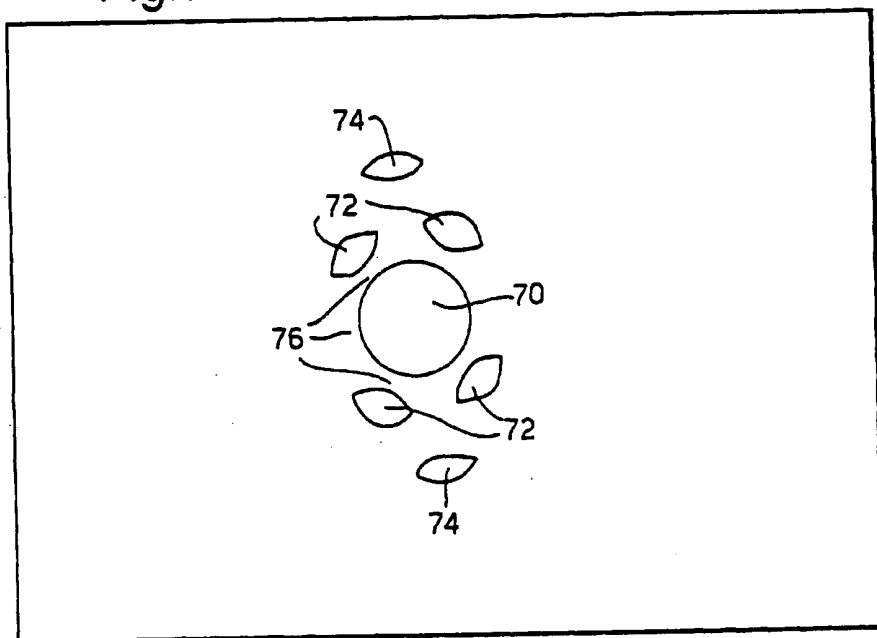


Fig.8.

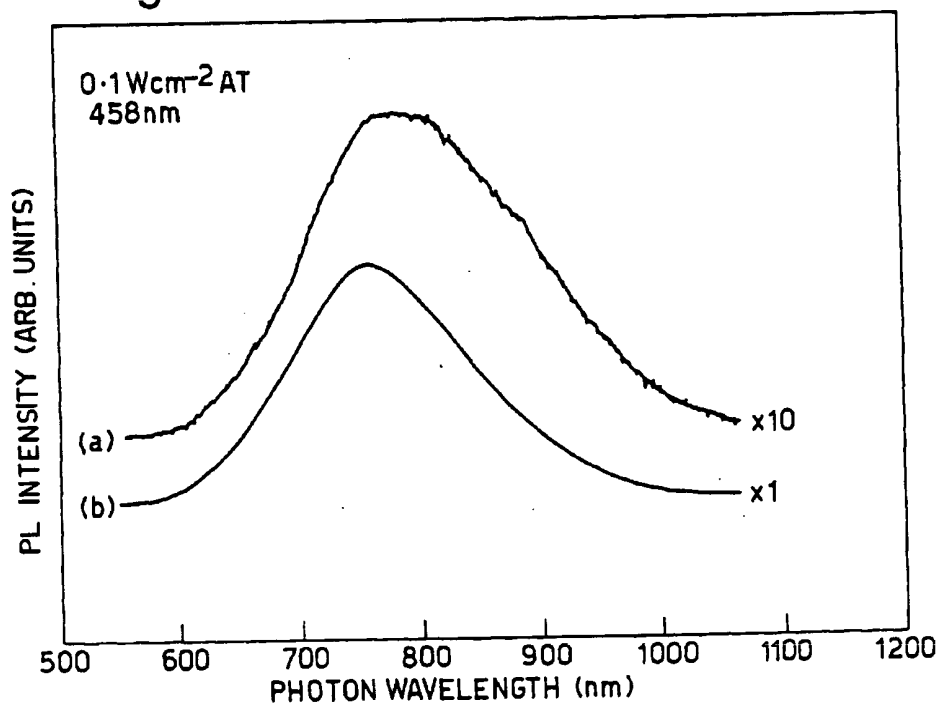


Fig.9.

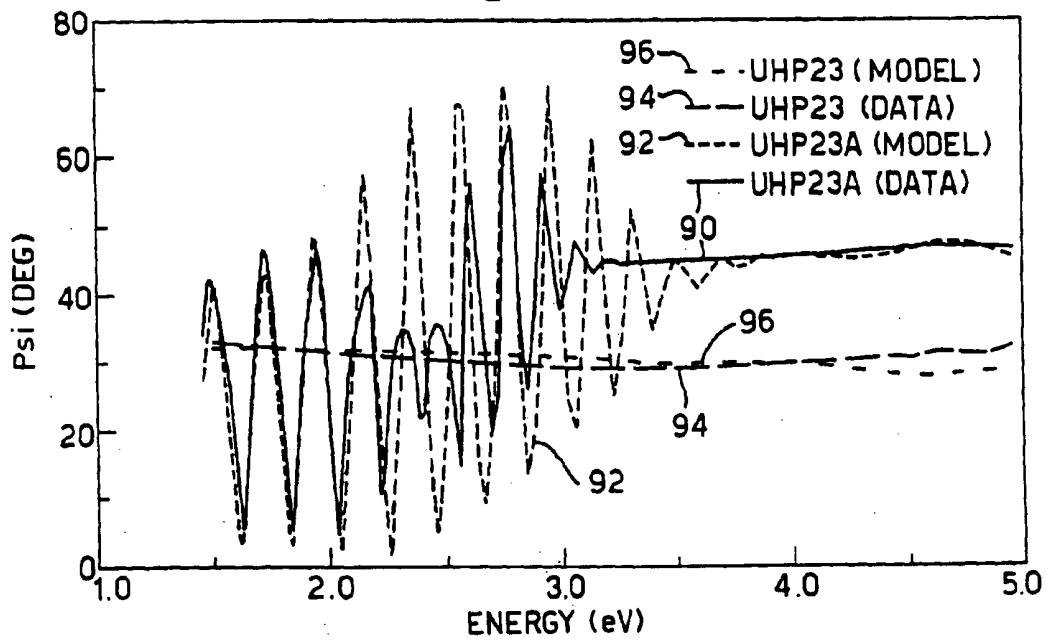


Fig.10.

